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FORM PTO-1390 (Modified)  
(REV 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES**

**220508US0PCT**

**DESIGNATED/ELECTED OFFICE (DO/EO/US)**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

**CONCERNING A FILING UNDER 35 U.S.C. 371**

**10/088517**

INTERNATIONAL APPLICATION NO.

**PCT/EP00/10684**

INTERNATIONAL FILING DATE

**31 October 2000**

PRIORITY DATE CLAIMED

**11 November 1999**

TITLE OF INVENTION

**CARBODIIMIDES CONTAINING CARBOXYL OR CARBOXYLATE GROUPS**

APPLICANT(S) FOR DO/EO/US

**Karl HABERLE et al.**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☒ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

**Items 13 to 20 below concern document(s) or information included:**

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

**Notice of Priority/ Form PTO-1449  
PCT/IB/304/ PCT/IB/308**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.53) <b>10 088517</b>		INTERNATIONAL APPLICATION NO. <b>PCT/EP00/10684</b>		ATTORNEY'S DOCKET NUMBER <b>220508US0PCT</b>	
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*24. The following fees are submitted: <b>BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5)) :</b> <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... <b>\$1040.00</b> <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... <b>\$890.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... <b>\$740.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... <b>\$710.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... <b>\$100.00</b> <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>CALCULATIONS PTO USE ONLY</b>	
				<b>\$890.00</b>	
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				<b>\$0.00</b>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	11 - 20 =	0	x \$18.00	<b>\$0.00</b>	
Independent claims	1 - 3 =	0	x \$84.00	<b>\$0.00</b>	
Multiple Dependent Claims (check if applicable) <input type="checkbox"/>				<b>\$0.00</b>	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$890.00</b>	
<input type="checkbox"/> Applicant claims small entity status. Sec 37 CFR 1.27). The fees indicated above are reduced by 1/2.				<b>\$0.00</b>	
<b>SUBTOTAL =</b>				<b>\$890.00</b>	
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				<b>\$0.00</b>	
<b>TOTAL NATIONAL FEE =</b>				<b>\$890.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$890.00</b>	
				Amount to be: refunded	\$
				charged	\$

a. ☒ A check in the amount of **\$890.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.


c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **15-0030**. A duplicate copy of this sheet is enclosed.

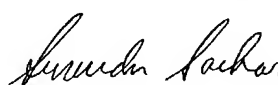
d. ☐ Fees are to be charged to a credit card. **WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.**

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:

**Surinder Sachar**  
**Registration No. 34,423**

  
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 SIGNATURE

**Norman F. Oblon**  
 NAME

**24,618**  
 REGISTRATION NUMBER

**March 29 2002**  
 DATE

220508US-0 PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :  
KARL HAEBERLE ET AL : ATTN: APPLICATION DIVISION  
SERIAL NO: NEW U.S. PCT APPLN :  
(BASED ON PCT/EP00/10684)  
FILED: HEREWITH :  
FOR: CARBODIIMIDES CONTAINING  
CARBOXYL OR CARBOXYLATE  
GROUPS

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please amend the claims as shown in the marked-up copy following this amendment to read as follows.

3. (Amended) A compound (V) as claimed in claim 1, wherein component (a) comprises hexamethylene diisocyanate or 1,3-bis(1-methyl-1-isocyanatoethyl)benzene.

4. (Amended) A compound (V) as claimed in claim 1, wherein the amino carboxylic acids and/or amino carboxylic salts comprise  $\alpha$ - or  $\beta$ -amino carboxylic acids, or the Michael adducts of diprimary diamines with  $\alpha,\beta$ -unsaturated carboxylic acids or carboxylic salts.

5. (Amended) A compound (V) as claimed in claim 1, wherein component (c) comprises aromatic compounds, aliphatic compounds or araliphatic compounds, the araliphatic compounds carrying polyalkylene oxide groups if desired, said compounds having 1 to 20 carbon atoms (not including the carbon atoms of the polyalkylene oxide groups) and having at least one functional group selected from the group consisting of secondary amino group, primary amino group and alcoholic hydroxyl group.

6. (Amended) A process for preparing a compound (V) as claimed in claim 1, which comprises

I. preparing carbodiimides having terminal isocyanate groups by carbodiimidizing some of the isocyanate groups of component (a), and

II. reacting the isocyanato-terminal compounds prepared in step I with component (b) and, if desired, with components (c) and (d).

7. (Amended) A mixture of a compound (V) as claimed in claim 1 and an aqueous dispersion comprising a polymer (P).

11. (Amended) An article adhesively bonded or coated with a mixture as claimed in claim 7, or a textile impregnated with said mixture.

REMARKS

Claims 1-11 are active in the present application. Claims 3-7 and 11 have been amended to remove multiple dependencies. No new matter is added. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
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**Marked-Up Copy**

Serial No: \_\_\_\_\_

Amendment Filed on: \_\_\_\_\_

3-29-2002

IN THE CLAIMS

--3. (Amended) A compound (V) as claimed in claim 1 [or 2], wherein component (a) comprises hexamethylene diisocyanate or 1,3-bis(1-methyl-1-isocyanatoethyl)benzene.

4. (Amended) A compound (V) as claimed in [any of claims 1 to 3] claim 1, wherein the amino carboxylic acids and/or amino carboxylic salts comprise  $\alpha$ - or  $\beta$ -amino carboxylic acids, or the Michael adducts of diprimary diamines with  $\alpha,\beta$ -unsaturated carboxylic acids or carboxylic salts.

5. (Amended) A compound (V) as claimed in [any of claims 1 to 4] claim 1, wherein component (c) comprises aromatic compounds, aliphatic compounds or araliphatic compounds, the araliphatic compounds carrying polyalkylene oxide groups if desired, said compounds having 1 to 20 carbon atoms (not including the carbon atoms of the polyalkylene oxide groups) and having at least one functional group selected from the group consisting of secondary amino group, primary amino group and alcoholic hydroxyl group.

6. (Amended) A process for preparing a compound (V) as claimed in [any of claims 1 to 5] claim 1, which comprises

I. preparing carbodiimides having terminal isocyanate groups by carbodiimidizing some of the isocyanate groups of component (a), and

II. reacting the isocyanato-terminal compounds prepared in step I with component (b) and, if desired, with components (c) and (d).

7. (Amended) A mixture of a compound (V) as claimed in [any of claims 1 to 5] claim 1 and an aqueous dispersion comprising a polymer (P).

11. (Amended) An article adhesively bonded or coated with a mixture as claimed in [any of claims 7 to 9] claim 7, or a textile impregnated with said mixture.--

Carbodiimides containing carboxyl or carboxylate groups

The invention relates to compounds containing carbodiimide units  
5 and carboxyl or carboxylate groups (compounds V), derived from

- a) aliphatic or araliphatic C<sub>4</sub> to C<sub>20</sub> polyisocyanates (component  
a)
- 10 b) amino carboxylic acids or amino carboxylic salts (component  
b) and
- c) if desired, further compounds which carry groups able to  
react with isocyanate groups in an addition reaction  
15 (component c)
- d) if desired, other isocyanates (component d),

the carbodiimide units deriving essentially exclusively from the  
20 isocyanate groups of component (a).

Organic carbodiimides and their use as additives to aqueous  
polymer dispersions are known. It is also known that these  
polymer dispersions, for example, are added in order to increase  
25 the molecular weight of the polymers. To permit the carbodiimides  
to be dispersed simply and homogeneously in the dispersion, they  
are provided with hydrophilic groups.

EP-A-198 343 describes carbodiimides which carry sulfonate groups  
30 and, if desired, polyethylene oxide units as well.

EP-A-686 626, furthermore, discloses carbodiimides in which the  
hydrophilicity is brought about by means of ammonium groups,  
which are introduced by way of dialkylamino alcohols, by means of  
35 sulfonate groups which are introduced by way of salts of  
hydroxy-functional alkylsulfonic acids, or by means of  
polyethylene oxide radicals.

The abovementioned products, however, have the following  
40 disadvantages:

Cationic products such as carbodiimides hydrophilicized by  
ammonium groups are not compatible with the anionically  
stabilized dispersions commonly used.



## 2

The carbodiimides hydrophilicized with sulfonate groups are difficult to prepare. Because of the highly lipophobic character of the salts used as starting compounds, the reaction with the hydrophobic isocyanato-containing precursors is extremely  
5 difficult, since the mutual solubility is very low.

The dispersions cured with carbodiimides hydrophilicized with polyalkylene oxide radicals possess a permanent hydrophilicity which is unwanted.

10 DE-A-19821668, unpublished at the priority date of the present specification, discloses carbodiimides based on 1,3-bis(1-methyl-1-isocyanatoethyl)benzene in which the hydrophilicization is brought about with amino sulfonic acids.

15 It is an object of the present invention to provide carbodiimides which are compatible with the customary, anionically stabilized polymer dispersions, are easy to prepare, and do not impart any additional, permanent hydrophilicity to the dispersion films  
20 cured with them.

The compounds (V) contain preferably from 200 to 2000 mmol/kg, with particular preference from 500 to 1800 mmol/kg, of carboxyl or carboxylate groups, based on the weight of the carbodiimides.

25 The proportion of carbodiimide groups is generally from 0.05 to 8, preferably from 0.10 to 5, mol/kg based on the weight of the carbodiimides.

30 The carbodiimide units in the carbodiimides of the invention are formed essentially by the combination of pairs of NCO groups of component (a) with elimination of carbon dioxide, so forming a carbodiimide.

35 The compounds (V) contain preferably at least one carbodiimide structure, preferably more than one carbodiimide structure; with particular preference, the (number-)average degree of condensation, i.e., the average number of carbodiimide structures in the carbodiimides of the invention, is from 1 to 20, in  
40 particular from 2 to 15.

Suitable monomers (a) are the aliphatic or araliphatic isocyanates having 4 to 20 carbon atoms that are commonly used in polyurethane chemistry.

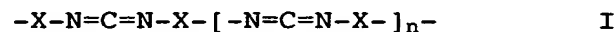
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## 3

Mention may be made in particular of diisocyanates  $X(NCO)_2$ , where X is an aliphatic hydrocarbon radical having 4 to 12 carbon atoms, a cycloaliphatic hydrocarbon radical having 6 to 15 carbon atoms, or an araliphatic hydrocarbon radical having 7 to 15

5 carbon atoms. Examples of diisocyanates of this kind are tetramethylenediisocyanate, hexamethylenediisocyanate, dodecamethylenediisocyanate, 1,4-diisocyanatocyclohexane, 1-isocyanato-3,5,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI), 2,2-bis(4-isocyanatocyclohexyl)propane, trimethylhexane  
10 diisocyanate, 1,4-diisocyanatobenzene, 1,3-bis(1-methyl-1-isocyanatoethyl)benzene (TMXDI), the isomers of bis(4-isocyanatocyclohexyl)methane (HMDI) such as the trans/trans, the cis/cis and the cis/trans isomer, and mixtures of these compounds.

15 The carbodiimides of the invention therefore preferably comprise units of the formula I



20 where

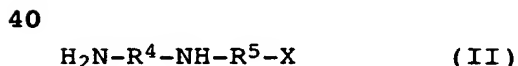
X is as defined above, and

25 n is an integer from 0 to 10, preferably 0, 1, 2 or 3.

With particular preference, X is derived from TMXDI or hexamethylenediisocyanate.

30 Suitable amino carboxylic acids and salts thereof (component B) are, for example, the alpha-amino carboxylic acids specified in Fieser and Fieser, Organische Chemie, 2nd, improved edition, 1982, on p. 1260 ff.; preferably: beta-amino carboxylic acids such as  $\beta$ -alanine or the Michael adducts of diprimary diamines  
35 with  $\alpha,\beta$ -unsaturated carboxylic acids. Where the amino carboxylic acids are used in the form of their salts, particularly suitable salts are alkali metal, alkaline earth metal, or ammonium salts.

Such compounds conform, for example, to the formula (II)



where

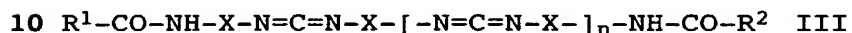
45 -  $R^4$  and  $R^5$ , independently of one another, are a  $C_1$  to  $C_6$  alkanediyl unit, preferably ethylene,

## 4

and X is COOH or a carboxylate group.

Particularly preferred compounds of the formula (II) are N-(2-aminoethyl)-2-aminoethanecarboxylic acid and the  
5 corresponding alkali metal salts, Na being the particularly preferred counterion.

Preferred compounds (V) are those of the formula III



where n and X are as defined for formula I and  $R^1$  and  $R^2$  are radicals derived from component (b) by abstracting therefrom a hydrogen atom attached to an amino group.

15 The compounds (V) may, if desired, further comprise, in addition to the structural units derived from components (a) and (b), further structural units which are derived from components (c) and (d) and which comprise primarily urethane units or urea  
20 units. These units are formed by reacting the isocyanate groups of the component (d) with the isocyanate-reactive groups of component (c) or with the amino groups of component (b) or by reacting isocyanate-reactive groups of component (c) with the isocyanate groups of component (a). By means of the structural  
25 units derived from components (c) and (d), therefore, the structural units of the formula I are interrupted or terminated or are located between a structural unit formed from component (a) and (b). Components (c) and (d) thus serve primarily to regulate the molecular weight, since components (c) and (d) act  
30 primarily as chain extenders or chain terminators.

Components (c) carry groups which are able to react with isocyanate groups in an addition reaction. For example, standard substances may be used which by virtue of their reaction with  
35 isocyanates produce urethane groups or urea groups. For example, aromatic, aliphatic or araliphatic compounds having 1 to 20 carbon atoms may be used whose isocyanate-reactive groups comprise hydroxyl and/or amino groups. Preferred compounds having at least two isocyanate-reactive groups are organic compounds  
40 having at least two hydroxyl groups, having at least two amino groups and/or having at least one hydroxyl group and at least one amino group. Examples which may be used include the following: aromatic, araliphatic and/or aliphatic polyols having 2 to 20 carbon atoms, preferably those having primary hydroxyl groups.  
45 Examples that may be mentioned include: 1,2-ethanediol, 1,3-propanediol, 1,2-propanediol, 1,4-butanediol, 2,4-butanediol and/or 2,3-butanediol, 1,5-pentanediol, 1,6-hexanediol,

$$= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-t^2} dt = 1$$
[illegible]
$$= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-t^2} dt = 1$$
[illegible][illegible][illegible]

the invention, especially if the diisocyanates are reacted to the carbodiimides in a first step and then the isocyanato-containing carbodiimides are reacted with the isocyanate-reactive compounds.

Component (b) is preferably used with monofunctional compounds, with particular preference with monoamines.

35 In general, the amount of components (c) and (d) as a proportion of all components (a) to (d) used to prepare the compounds V is not more than from 0 to 40%, preferably from 0 to 30% by weight.

I. preparing carbodiimides having terminal isocyanate groups by carbodiimidizing some of the isocyanate groups of component (a), and

## 7

II. reacting the isocyanato-terminal compounds prepared in step I with component (b) and, if desired, with components (c) and (d).

5 In step I, carbodiimide structures are produced by the familiar reaction of the isocyanate groups with one another, with elimination of carbon dioxide, in the presence of customary catalysts known for this reaction. In step II, isocyanate groups are reacted with isocyanate-reactive compounds, in a known  
10 manner, to prepare urethane and/urea structures.

The molar ratio of the NCO groups of the isocyanate-containing carbodiimide to the sum of the isocyanate-reactive groups of component (c) and the amino groups of component (a) is usually  
15 from 10:1 to 0.2:1, preferably from 5:1 to 0.5:1.

Alternatively, the carbodiimides of the invention may be obtained by first reacting component (a) with components (b) and, if desired, (c), the ratio of isocyanate groups used to the sum of  
20 the isocyanate-reactive groups of component (c) and the amino groups of component (b) being at least 2:1, and then reacting the isocyanato-containing reaction product in the presence of catalysts, with release of carbon dioxide, to give carbodiimides. In accordance with this process variant, up to 50% by weight,  
25 preferably up to 23% by weight, of the isocyanate groups of component (a) are first reacted with the isocyanate-reactive compounds and then some or all of the free isocyanate groups are reacted in the presence of catalysts, with release of carbon dioxide, to give carbodiimide groups.

30

The reactions may preferably be conducted in the presence of a solvent and, if desired, a solubilizing auxiliary solvent, with particular preference in the presence of a solvent and a solubilizing auxiliary solvent. A suitable solvent is preferably  
35 water. Suitable solubilizing auxiliary solvents are, in particular, those compounds which readily dissolve the product of the reaction of step I and are also miscible with water, examples being methanol, ethanol, n- and/or isopropanol, propanone, tetrahydrofuran, dioxane, N-methylpyrrolidone, dimethylformamide,  
40 dimethylacetamide and/or propylenecarbonate. It is preferred to use auxiliary solvents having a boiling point at 1013 mbar of <100°C. The weight ratio of solvent to auxiliary solvent is usually from 50:1 to 0.02:1.

45 The reaction of the water and also of the alcoholic auxiliary solvents with the isocyanate groups is relatively slow compared with that of the amino group of component (b). Free amino

The temperature during the step in which predominantly urethane groups and urea groups are formed is usually from 10 to 100°C.

The compound (V) of the invention is suitable in particular for  
45 increasing the molecular weight of the polymers (P) which are  
present in the form of an aqueous dispersion.

Mixtures of compounds (V) and aqueous dispersions comprising polymer (P) contain compounds (V) and polymer (P) preferably in a ratio of from 0.005:1 to 1:1.

The mixing operation is not critical and may be performed, for example, by stirring compound (V) into the aqueous dispersions comprising polymer (P). The mixing operation may take place at any desired point in time prior to use of said dispersions.

Examples of suitable polymers (P) are water-dispersible polyurethanes (polymers PII). Polyurethanes of this kind and the dispersions comprising them are general knowledge (cf. Ullmann's Encyclopedia of Industrial Chemistry, 5<sup>th</sup> Edition, Volume A 21, pages 677 f.).

IIa) diisocyanates having 4 to 30 carbon atoms,

I Ib) diols of which

30

IIb2) from 0 to 90 mol%, based on the total amount of the diols (IIb), have a molecular weight of from 60 to 500 g/mol,

IIc) monomers different than the monomers (IIa) and (IIb) and containing at least one isocyanate group or at least one isocyanate-reactive group, and further carrying at least one hydrophilic group or potentially hydrophilic group, thereby rendering the polyurethanes dispersible in water,

IIId) if desired, further polyfunctional compounds different than the monomers (IIa) to (IIc) and having reactive groups which comprise alcoholic hydroxyl groups, primary or secondary amino groups or isocyanate groups, and



IIe) if desired, monofunctional compounds different than the monomers (IIa) to (IId) and having a reactive group which comprises an alcoholic hydroxyl group, a primary or secondary amino group or an isocyanate group.

Suitable monomers (IIa) are the aliphatic or aromatic diisocyanates commonly used in polyurethane chemistry. Preference is given to the monomers (IIa), or mixtures thereof, which are also mentioned as monomers (IIa) in DE-A-19521500.

Suitable monomers (IIb) and (IIc) are preferably the monomers (IIb) and (IIc) mentioned in DE-A-19521500.

Monomers IIb1 are, for example, polyesterdiols or polyether

Monomers IIb2 are, for example, aliphatic diols having 2 to 12 carbon atoms, e.g., 1,4-butanediol or 1,6-hexanediol.

Suitable monomers (IIId) are, for example, aliphatic amines having 2 to 12 carbon atoms and 2 to 4 primary and/or secondary amino groups. Examples are ethylenediamine, isophorone diamine, and diethylenetriamine.

In order to ensure that the polyurethanes are dispersible in water, the polyurethanes are synthesized not only from components (IIa), (IIb) and (IIc) but also from monomers (IIc), which are different than components (IIa), (IIb) and (IIc), carry at least one isocyanate group or at least one isocyanate-reactive group, and also carry at least one hydrophilic group or group convertible to a hydrophilic group. In the text below, the term "hydrophilic groups or potentially hydrophilic groups" is abbreviated to "(potentially) hydrophilic groups". The (potentially) hydrophilic groups react with isocyanates substantially more slowly than do the functional groups of the monomers used to synthesize the polymer main chain.

Preferred monomers (IIc) are likewise the monomers referred to as monomers (IIc) in DE-A-19521500.

The amount of components having (potentially) hydrophilic groups as a proportion of the total amount of components (IIa), (IIb), (IIc), (II d) and (IIe) is generally such that the molar amount of the (potentially) hydrophilic groups, based on the amount by weight of all monomers (a) to (e), is from 80 to 1200, preferably

## 11

from 140 to 1000, and with particular preference from 200 to 800, mmol/kg.

- The (potentially) hydrophilic groups may comprise nonionic groups, e.g., polyethylene oxide groups, or, preferably, (potentially) ionic hydrophilic groups, e.g., carboxylate groups or sulfonate groups. It is preferred to operate without effective amounts of nonionic groups.
- 10 The proportion of nonionic hydrophilic groups, if such are incorporated, is in general up to 5, preferably up to 3, with particular preference up to 1% by weight, based on the amount by weight of all monomers (IIa) to (IIe).
- 15 Monomers (IIe), which are used if desired, are monoisocyanates, monoalcohols, and mono-primary and mono-secondary amines. In general their proportion is not more than 10 mol%, based on the total molar amount of the monomers. These monofunctional compounds usually carry further functional groups such as
- 20 carbonyl groups and are used to introduce into the polyurethane functional groups which permit the dispersing and/or crosslinking or further polymer-analogous reaction of the polyurethane.

In the field of polyurethane chemistry it is general knowledge as to how the molecular weight of the polyurethanes may be adjusted by choosing the proportions of the co-reactive monomers and also the arithmetic mean of the number of reactive functional groups per molecule.

- 30 Normally, the components (IIa) to (IIe) and their respective molar amounts are chosen such that the ratio A:B, where

A) is the molar amount of isocyanate groups, and

- 35 B) is the sum of the molar amount of the hydroxyl groups and the molar amount of the functional groups which are able to react with isocyanates in an addition reaction,

is from 0.5:1 to 2:1, preferably from 0.8:1 to 1.5, with particular preference from 0.9:1 to 1.2:1. With very particular preference, the ratio A:B is as close as possible to 1:1.

Furthermore, the proportion of the monomers (a) is preferably chosen such that the amount of the monomers (IIa) as a proportion of the monomers (IIa) to (IIe) is from 20 to 70% by weight.

The monomers (IIa) to (IIe) that are used carry on average usually from 1.5 to 2.5, preferably from 1.9 to 2.1, with particular preference from 2.0, isocyanate groups and/or functional groups which are able to react with isocyanates in an addition reaction.

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15

IIIa) from 30 to 99.9% by weight of principal monomers selected from C<sub>1</sub> to C<sub>20</sub> alkyl(meth)acrylates, vinyl esters of carboxylic acids containing up to 20 carbon atoms, vinylaromatic compounds having up to 20 carbon atoms, ethylenically unsaturated nitriles, vinyl halides, and aliphatic hydrocarbons having 2 to 8 carbon atoms and 1 or 2 double bonds,

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Examples of nitriles are acrylonitrile and methacrylonitrile.

The vinyl halides are chlorine-, fluorine- or bromine-substituted, ethylenically unsaturated compounds, preferably vinyl chloride and vinylidene chloride.

- 5 Nonaromatic hydrocarbons that may be mentioned having 2 to 8 carbon atoms and one or two olefinic double bonds are butadiene, isoprene and chloroprene, and also ethylene, propylene and isobutylene.
- 10 The principal monomers (IIIa) are also used preferably in a mixture.

- Vinylaromatic compounds such as styrene are frequently used, for example, in a mixture with C<sub>1</sub>-C<sub>20</sub>-alkyl (meth)acrylates, in particular with C<sub>1</sub>-C<sub>8</sub>-alkyl (meth)acrylates, or with nonaromatic hydrocarbons such as isoprene, or, preferably, butadiene.

Suitable monomers (IIIb) are preferably (meth)acrylic acid or maleic acid.

- 20 Examples of suitable monomers (IIIc) are the following: esters of acrylic and methacrylic acid with alcohols having 1 to 20 carbon atoms, which in addition to the oxygen atom in the alcohol group contain a least one further heteroatom and/or contain an
- 25 aliphatic or aromatic ring, such as 2-ethoxyethyl acrylate, 2-butoxyethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, (meth)acrylic aryl, alkaryl or cycloalkyl esters, such as cyclohexyl (meth)acrylate, phenyl ethyl (meth)acrylate, phenylpropyl (meth)acrylate, or acrylic
- 30 esters of heterocyclic alcohols such as furyl (meth)acrylate.

- Furthermore, suitable monomers (IIIc) are also monomers having amino groups or amide groups, such as (meth)acrylamide, and also the derivatives thereof substituted on the nitrogen by C<sub>1</sub>-C<sub>4</sub> alkyl.

Of particular importance as monomers (IIIc) are hydroxy-functional monomers, examples being (meth)acrylic acid C<sub>1</sub>-C<sub>15</sub> alkyl esters substituted by one or two hydroxyl groups.

- 40 Particularly significant hydroxy-functional comonomers are (meth)acrylic acid C<sub>2</sub>-C<sub>8</sub> hydroxyalkyl esters, such as n-hydroxyethyl, n-hydroxypropyl, or n-hydroxybutyl (meth)acrylate.

## 14

The polymer (PIII) is prepared by free-radical addition polymerization. Appropriate polymerization methods, such as bulk, solution, suspension or emulsion polymerization, are known to the skilled worker.

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The copolymer is preferably prepared by solution polymerization with subsequent dispersion in water or, with particular preference, by emulsion polymerization.

- 10 In the case of the emulsion polymerization, the comonomers can be polymerized in a customary manner in the presence of water-soluble initiator and an emulsifier at preferably from 30 to 95°C.

- 15 Examples of suitable initiators are sodium, potassium and ammonium persulfate, tert-butyl hydroperoxides, water-soluble azo compounds, or redox initiators.

- Examples of emulsifiers used are alkali metal salts of relatively  
20 long-chain fatty acids, alkyl sulfates, alkylsulfonates, alkylated arylsulfonates, or alkylated biphenyl ether sulfonates. Further suitable emulsifiers are reaction products of alkylene oxides, especially ethylene oxide or propylene oxide, with fatty alcohols, fatty acids or phenols, and/or alkyl phenols.

25

- In the case of aqueous secondary dispersions, the copolymer is prepared first by solution polymerization in an organic solvent and is subsequently dispersed in water without the use of an emulsifier or dispersing auxiliary but with the addition to  
30 copolymers containing carboxylic acid groups of salt formers, e.g., ammonia. The organic solvent may be removed by distillation. The preparation of aqueous secondary dispersions is known to the skilled worker and is described, for example, in DE-A-37 20 860.

35

- In order to adjust the molecular weight, regulators may be used. Appropriate examples are -SH-containing compounds such as mercaptoethanol, mercaptopropanol, thiophenol, thioglycerol, ethyl thioglycolate, methyl thioglycolate, and tert-dodecyl  
40 mercaptan, which may be used additionally in amounts, for example, of from 0 to 0.5% by weight, based on the copolymer.

- The nature and amount of the comonomers is preferably chosen such that the resulting copolymer has a glass transition temperature  
45 of from -60 to +140°C, preferably from -60 to +100°C. The glass transition temperature of the copolymer is determined by means of

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differential thermoanalysis or differential scanning calorimetry in accordance with ASTM 3418/82.

The number-average molecular weight  $M_n$  is preferably from  $10^3$  to  $5 \cdot 10^6$ , with particular preference from  $10^5$  to  $2 \cdot 10^6$  g/mol (determined by gel permeation chromatography using polystyrene as the standard).

The polymers (P) may further comprise (polymers PIV) a water-dispersible polyester which carries carboxyl groups.

The water-dispersible polyesters which carry carboxyl groups (polymer IV) are known, for example, from Encyclopedia of polymer science and engineering, John Wiley & Sons, second edition, volume 12, pages 300 to 313.

The aqueous dispersions comprising the polymer (P) usually have a solids content of from 10 to 70% by weight.

The mixtures of the invention comprising compound (V) and polymer (P) may comprise commercially customary auxiliaries and additives such as wetting agents, defoamers, flatting agents, emulsifiers, thickeners and thixotropic agents, and colorants such as dyes and pigments.

25

They are suitable, for example, for the adhesive bonding or coating of different substrates such as wood, metal, plastics, paper, leather or textile, for the impregnation of textiles, and for the production of moldings and printing inks.

30

The polyurethane dispersions of the invention may be processed by the processes widespread in the adhesives, leather or coatings industry; i.e., by spraying, rolling or knife-coating the dispersions onto the substrate and then drying them.

35

Where the dispersions are processed as adhesives, the coated workpieces are joined to another workpiece, preferably with application of pressure, either before the dispersion film has dried or after drying.

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Particularly firm adhesive bonds are obtained if workpieces that have been provided with a dried adhesive film are heated to a temperature of from about 50 to 100°C directly before, during or after joining.

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## 16

The adhesive bonds produced by these methods are particularly notable for the fact that they are stable on storage and possess high thermal stability.

## 5 Experimental section

## 1. Preparation of a hydrophilic polycarbodiimide

110 g of an NCO-terminated carbodiimide made from TMXDI and  
10 having an NCO content of 7.8% by weight were introduced with stirring into a solution of 8 g of NaOH pellets and 17.8 g of beta-alanine in 80 g of water and 150 g of acetone. After 120 minutes of stirring at 50°C, the acetone was stripped off under reduced pressure and the mixture was diluted with 170 g of water.  
15 A colloidal, aqueous solution of a carbodiimide having a solids content of 34% and an LT of 100 is obtained.

Use Example 1: Utility as adhesive

20 First of all, a polyurethane dispersion was prepared. 594 g of a polyester diol made from isophthalic acid, adipic acid and hexane diol (OHZ=56.6) and 40.2 g of dimethylolpropionic acid in 200 g of acetone were admixed with 0.5 g of DBTL and 60.9 g of TDI and 58.9 g of HDI were metered in at 60°C. After 6 h 40 min at  
25 65-68°C, the mixture was diluted with 700 g of acetone and cooled to 50°C. The NCO content was now 0.54%. The mixture was neutralized with 9.6 g of 50% strength NaOH and diluted with 40 g of DI water. After 10 minutes, the mixture was dispersed with 950 g of DI water. The acetone was distilled off in vacuo at  
30 100 mbar and 43°C, and the solids content was adjusted to approximately 40%.

SC: 39.7% LT: 94 pH: 6.4 Visc.: 79 mPas K value: 47

## 35 Use Example 1.1:

150 g of the PU dispersion from Use Example 1 are mixed with 22.2 g of the CDI solution from 1.

## 40 Use Example 1.2:

150 g of the PU dispersion from Use Example 1 are mixed with 11.1 g of the CDI solution.

## 45 Use Example 1.3:

## 17

150 g of the PU dispersion from Use Example 1 are used without CDI solution.

## 1.4 Performance testing

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The mixtures were subjected to RF/PVC bonding and the heat stability was measured

## 1.4.1 Preparation of the test specimens

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The tests were carried out in accordance with the following test specifications:

- 15 Substrate: Rigid fiberboard/PVC sheet, type: Benecke 577/E28
- Dimensions: 200 x 200 mm
- 20 Bonding area: 200 x 170 mm (subdivided into 5 test strips each measuring 30 mm)
- Application: 2 mm wire-wound coating bar onto rigid fiberboard in lengthwise direction
- 25 Drying: 3 min at 60°C
- Mode of bonding: Hot pressing at 80°C, PVC side only
- Pressing pressure: 0.1 N/mm<sup>2</sup>
- 30 Pressing duration: 30 s
- Sample storage:: 1 day at RT
- 35 Test load: 300 g per 30 mm wide test strip
- Peel angle: 180°
- Number of samples: 1 plate = 5 samples
- 40 1.4.2 Load testing and evaluation
- The tests were carried out in accordance with the following test specifications:

45



Following application of the adhesive, drying and pressing, 30 mm wide strips with an interval of 10 mm in between are cut from the area produced in this way. When cutting, it is only the sheet which is separated; the rigid fiberboard remains undamaged. The 10 mm wide strips in between are removed and a 300 g weight is clamped to each of the 30 mm wide test strips.

The test begins at 40°C. At intervals of 30 minutes the temperature is raised by 10°C. In the heating phase, which lasts 10 15 minutes, the test strips are not loaded.

Assessment of the fracture type:

C = separation in the adhesive film without detachment from one  
15 material (cohesive fracture)

### 1.4.3 Results:

An evaluation is made of the temperature, measured in °C, at which  
20 the bond still holds.

If there is more than 10 mm of peeling, the test is finished.

The test results are summarized in Table 1.

Table 1

Experiment	HS
Example 1.1	2x 110°C, 3x 120°C
Example 1.2	1x 110°C, 4x 120°C
Example 1.2	6x 90°C

Use Example 2

### Preparation of a polyacrylate dispersion

35 To 200 g of deionized water in a 2 l reactor there were added, at 85°C, 6 g of a solution of 2 g of sodium persulfate in 68 g of water (feed stream 2) and 15.5 g of an emulsion of 370 g of styrene, 400 g of n-butyl acrylate, 21 g of acrylic acid, 16 g of  
40 a 50% aqueous solution of acrylamide, 32 g of a 20% aqueous solution of an ethoxylated (n = 18) saturated linear C<sub>16</sub>C<sub>18</sub> fatty alcohol and 12 g of a 45% aqueous solution of the sodium salt of the disulfonic acid of a dodecyl-substituted diphenyl ether in 470 g of water (feed stream 1), and this mixture was initially  
45 polymerized for 30 minutes. Subsequently the remainders of feed streams 1 and 2 were added over 2 hours and over 2 hours 15 minutes, respectively. Polymerization was continued at 85°C for 2

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hours and then the product was neutralized with concentrated ammonia solution to a pH of 8.

SC 49%      pH: 8.0      LT: 23      Visc.: 1720 mPas

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Use Example 2.1:

150 g of the acrylate dispersion from Use Example 2 were diluted to a solids content of 25% and mixed with 2.5 g of the CDI

10 solution.

Use Example 2.2:

150 g of the acrylate dispersion from Use Example 2 were diluted to a solids content of 25% and mixed with 5 g of the CDI solution.

Use Example 2.3 (comparative):

20 150 g of the acrylate dispersion from Example 2 were diluted to a solids content of 25% and used without CDI solution.

Films 1 mm thick were cast from the dispersions of Use Example 2.1 to 2.3 and dried at room temperature for 14 days.

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#### 2.4 Testing

The films were subjected to a tensile test in accordance with DIN 53504.

30

The results are summarized in Table 2:

Table 2

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Use Example	Yield stress (MPa)	Elongation at break (%)
2.1.	7.2	430
2.2.	8.4	410
2.3. (Comparative)	6.2	320

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The increase in yield stress and elongation at break indicates crosslinking.

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We claim:

- 5 1. A compound containing carbodiimide units and carboxyl or  
carboxylate groups (compound V), derived from
- a) aliphatic or araliphatic C<sub>4</sub> to C<sub>20</sub> polyisocyanates (component  
a)
- 10 b) amino carboxylic acids or amino carboxylic salts (component  
b) and
- 15 c) if desired, further compounds which carry groups able to  
react with isocyanate groups in an addition reaction  
(component c)
- d) if desired, other isocyanates (component d),
- 20 the carbodiimide units deriving essentially exclusively from  
the isocyanate groups of component (a).
- 25 2. A compound (V) as claimed in claim 1, containing from 200 to  
2000 mmol/kg of carboxyl or carboxylate groups, based on the  
weight of the compound.
- 30 3. A compound (V) as claimed in claim 1 or 2, wherein component  
(a) comprises hexamethylene diisocyanate or  
1,3-bis(1-methyl-1-isocyanatoethyl)benzene.
- 35 4. A compound (V) as claimed in any of claims 1 to 3, wherein  
the amino carboxylic acids and/or amino carboxylic salts  
comprise  $\alpha$ - or  $\beta$ -amino carboxylic acids, or the Michael  
adducts of diprimary diamines with  $\alpha,\beta$ -unsaturated carboxylic  
acids or carboxylic salts.
- 40 5. A compound (V) as claimed in any of claims 1 to 4, wherein  
component (c) comprises aromatic compounds, aliphatic  
compounds or araliphatic compounds, the araliphatic compounds  
carrying polyalkylene oxide groups if desired, said compounds  
having 1 to 20 carbon atoms (not including the carbon atoms  
of the polyalkylene oxide groups) and having at least one  
functional group selected from the group consisting of

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secondary amino group, primary amino group and alcoholic hydroxyl group.

6. A process for preparing a compound (V) as claimed in any of  
5 claims 1 to 5, which comprises
- I. preparing carbodiimides having terminal isocyanate groups  
by carbodiimidizing some of the isocyanate groups of  
10 component (a), and
- II. reacting the isocyanato-terminal compounds prepared in  
step I with component (b) and, if desired, with  
components (c) and (d).
- 15 7. A mixture of a compound (V) as claimed in any of claims 1 to  
5 and an aqueous dispersion comprising a polymer (P).
8. A mixture as claimed in claim 7, wherein the polymer (P)  
20 carries carboxyl groups.
9. A mixture as claimed in claim 7, wherein polymer (P)  
comprises a polyurethane (PII) synthesized from
- 25 IIA) diisocyanates having 4 to 30 carbon atoms,  
IIB) diols of which
- IIB1) from 10 to 100 mol%, based on the total amount of  
30 the diols (IIB), have a molecular weight of from 500  
to 5000, and
- IIB2) from 0 to 90 mol%, based on the total amount of the  
diols (IIB), have a molecular weight of from 60 to  
35 500 g/mol,
- IIC) monomers different than the monomers (IIA) and (IIB) and  
containing at least one isocyanate group or at least one  
40 isocyanate-reactive group, and further carrying at least one  
hydrophilic group or potentially hydrophilic group, thereby  
rendering the polyurethanes dispersible in water,
- IID) if desired, further polyfunctional compounds different than  
45 the monomers (IIA) to (IIC) and having reactive groups which  
comprise alcoholic hydroxyl groups, primary or secondary

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## 23

Carbodiimides with carboxyl or carboxylate groups

## Abstract

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Compounds containing carbodiimide units and carboxyl or carboxylate groups (compounds V), derived from

- 10 a) aliphatic or araliphatic  $C_4$  to  $C_{20}$  polyisocyanates (component a)
- b) amino carboxylic acids or amino carboxylic salts (component b) and
- 15 c) if desired, further compounds which carry groups able to react with isocyanate groups in an addition reaction (component c)
- d) if desired, other isocyanates (component d),
- 20 the carbodiimide units deriving essentially exclusively from the isocyanate groups of component (a).

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# Declaration and Power of Attorney for Patent Application

## Erklärung für Patentanmeldungen mit Vollmacht

### German Language Declaration

Als nachstehend benannter Erfinder erkläre ich hiermit an Eides Statt:

Dass mein Wohnsitz, meine Postanschrift und meine Staatsangehörigkeit den im nachstehenden nach meinem Namen aufgeführten Angaben entsprechen, dass ich nach bestem Wissen der ursprüngliche, erste und alleinige Erfinder (falls nachstehend nur ein Name angegeben ist) oder ein ursprünglicher, erster und Miterfinder (falls nachstehend mehrere Namen aufgeführt sind) des Gegenstandes bin, für den dieser Antrag gestellt wird und für den ein Patent für die Erfindung mit folgendem Titel beantragt wird:

CARBODIIMIDES CONTAINING CARBOXYL OR CARBOXYLATE GROUPS

deren Beschreibung:

[ ] ist beigefügt

[ ] wurde angemeldet am \_\_\_\_\_

unter der US-Anmeldenummer oder unter der Internationalen Anmeldenummer im Rahmen des Vertrages über die Zusammenarbeit auf dem Gebiet des Patentwesens (PCT)

\_\_\_\_\_ und am

\_\_\_\_\_ abgeändert (falls zutreffend).

Ich bestätige hiermit, dass ich den Inhalt der oben angegebenen Patentanmeldung, einschließlich der Ansprüche, die eventuell durch einen oben erwähnten Zusatzantrag abgeändert wurde, durchgesehen und verstanden habe.

Ich erkenne meine Pflicht zur Offenbarung jeglicher Informationen an, die zur Prüfung der Patentfähigkeit in Einklang mit Titel 37, Code of Federal Regulations, § 1.56 von Belang sind.

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

the specification of which:

[ ] is attached hereto

[x] was filed on *31 October 2000*

\_\_\_\_\_ as United States Application Number or PCT International Application Number

*PCT/EP/00/10684* \_\_\_\_\_ and was amended on

\_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

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Prior foreign application(s)  
(Frühere ausländische Anmeldungen)

<u>19954500.6</u>	<u>Germany</u>
(Number)	(Country)
(Nummer)	(Land)

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(Application No.)	(Filing Date)
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I hereby claim foreign priority under Title 35, United States Code, § 119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below, and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority claimed

Priorität  
beansprucht

<u>11 November 1999</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Day/Month/Year filed)	Yes	No
(Tag/Monat/Jahr der Anmeldung)	Ja	Nein

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

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(Application No.)	(Filing Date)
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I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

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**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: *(list name and registration number)*



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## Declaration

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